

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C.20231.
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 16 September 1999 (16.09.99)	
International application No. PCT/EP98/08394	Applicant's or agent's file reference PB751/PCT/RS
International filing date (day/month/year) 21 December 1998 (21.12.98)	Priority date (day/month/year) 23 December 1997 (23.12.97)
Applicant JONES, Christopher, Raymond et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
16 July 1999 (16.07.99)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer F. Baechler Telephone No.: (41-22) 338.83.38
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PTO/PCT Rec'd 21 JUN 2000 Rgms
PCT

From the INTERNATIONAL BUREAU

NOTICE INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:

SAVIDGE, Roger, Gordon, Madgwick
Albright & Wilson UK Limited
210-222 Hagley Road West
Oldbury
West Midlands B68 0NN
ROYAUME-UNI

IMPORTANT NOTICE

Date of mailing (day/month/year)

08 July 1999 (08.07.99)

Applicant's or agent's file reference

PB751/PCT/RS *Midland*

International application No.

PCT/EP98/08394

International filing date (day/month/year)

21 December 1998 (21.12.98)

Priority date (day/month/year)

23 December 1997 (23.12.97)

Applicant

ALBRIGHT & WILSON UK LIMITED et al

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
- AU,CN,EP,IL,JP,KP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CU,CZ,DE,DK,EA,EE,ES,FI,GB,GD,GE,GH,GM,HR,HU,
ID,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MN,MW,MX,NO,NZ,OA,PL,PT,RO,RU,SD,
SE,SG,SI,SK,SL,TJ,TM,TR,TT,UA,UG,UZ,VN,YU,ZW

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 08 July 1999 (08.07.99) under No. WO 99/33345

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO
34, chemin des Colmbettes
1211 Geneva 20, Switzerland

Authorized officer

J. Zahra

Facsimile No. (41-22) 740.14.35

Telephone No. (41-22) 338.83.38

PCT

From the INTERNATIONAL BUREAU

To:

SAVIDGE, Roger, Gordon, Madgwick
Albright & Wilson UK Limited
210-222 Hagley Road West
Oldbury
West Midlands B68 0NN
ROYAUME-UNI

NOTIFICATION OF RECEIPT OF
RECORD COPY

(PCT Rule 24.2(a))

Date of mailing (day/month/year)

11 March 1999 (11.03.99)

IMPORTANT NOTIFICATION

Applicant's or agent's file reference

PB751/PCT/BS

International application No.

PCT/EP98/08394

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

ALBRIGHT & WILSON UK LIMITED (for all designated States except US)
JONES, Christopher, Raymond et al (for US)

International filing date

21 December 1998 (21.12.98)

Priority date(s) claimed

23 December 1997 (23.12.97)

14 March 1998 (14.03.98)

19 March 1998 (19.03.98)

03 June 1998 (03.06.98)

18 September 1998 (18.09.98)

Date of receipt of the record copy
by the International Bureau

24 February 1999 (24.02.99)

List of designated Offices

AP : GH, GM, KE, LS, MW, SD, SZ, UG, ZW

EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

EP : AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE

OA : BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG

National : AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO,
NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer:

Céline Faust

Facsimile No. (41-22) 740.14.35

Telephone No. (41-22) 338.83.38

Form PCT/IB/301 (July 1998)

002524500

NOTIFICATION OF RECEIPT OF RECORD COPY

Date of mailing (day/month/year) 11 March 1999 (11.03.99)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference PB751/PCT/RS	International application No. PCT/EP98/08394

ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

- ☒ time limits for entry into the national phase
- ☐ confirmation of precautionary designations
- ☐ requirements regarding priority documents

A copy of this Notification is being sent to the receiving Office and to the International Searching Authority.

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

T :

SAVIDGE, Roger, Gordon, Madgwick
Albright & Wilson UK Limited
210-222 Hagley Road West
Oldbury
West Midlands B68 0NN
ROYAUME-UNI

Date of mailing (day/month/year) 11 March 1999 (11.03.99)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference PB751/PCT/RS	
International application No. PCT/EP98/08394	
International publication date (day/month/year) Not yet published	
Applicant ALBRIGHT & WILSON UK LIMITED et al	International filing date (day/month/year) 21 December 1998 (21.12.98) Priority date (day/month/year) 23 December 1997 (23.12.97)

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An asterisk(*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
23 Dec 1997 (23.12.97)	9727006.0	GB	24 Febr 1999 (24.02.99)
14 Marc 1998 (14.03.98)	9805407.5	GB	24 Febr 1999 (24.02.99)
19 Marc 1998 (19.03.98)	9805746.6	GB	24 Febr 1999 (24.02.99)
03 June 1998 (03.06.98)	9811778.1	GB	24 Febr 1999 (24.02.99)
18 Sept 1998 (18.09.98)	9820255.9	GB	24 Febr 1999 (24.02.99)

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Céline Faust



Facsimile No. (41-22) 740.14.35

Telephone No. (41-22) 338.83.38

INFORMATION TIME LIMITS FOR ENTERING THE NATIONAL PHASE

The applicant is reminded that the "national phase" must be entered before each of the designated Offices indicated in the Notification of Receipt of Request Copy (Form PCT/IB/301) by paying national fees and furnishing translations, as prescribed by the applicable national laws.

The time limit for performing these procedural acts is **20 MONTHS** from the priority date or, for those designated States which the applicant elects in a demand for international preliminary examination or in a later election, **30 MONTHS** from the priority date, provided that the election is made before the expiration of 19 months from the priority date. Some designated (or elected) Offices have fixed time limits which expire even later than 20 or 30 months from the priority date. In other Offices an extension of time or grace period, in some cases upon payment of an additional fee, is available.

In addition to these procedural acts, the applicant may also have to comply with other special requirements applicable in certain Offices. It is the applicant's responsibility to ensure that the necessary steps to enter the national phase are taken in a timely fashion. Most designated Offices do not issue reminders to applicants in connection with the entry into the national phase.

For detailed information about the procedural acts to be performed to enter the national phase before each designated Office, the applicable time limits and possible extensions of time or grace periods, and any other requirements, see the relevant Chapters of Volume II of the PCT Applicant's Guide. Information about the requirements for filing a demand for international preliminary examination is set out in Chapter IX of Volume I of the PCT Applicant's Guide.

GR and ES became bound by PCT Chapter II on 7 September 1996 and 6 September 1997, respectively, and may, therefore, be elected in a demand or a later election filed on or after 7 September 1996 and 6 September 1997, respectively, regardless of the filing date of the international application. (See second paragraph above.)

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

CONFIRMATION OF PRECAUTIONARY DESIGNATIONS

This notification lists only specific designations made under Rule 4.9(a) in the request. It is important to check that these designations are correct. Errors in designations can be corrected where precautionary designations have been made under Rule 4.9(b). The applicant is hereby reminded that any precautionary designations may be confirmed according to Rule 4.9(c) before the expiration of 16 months from the priority date. If it is not confirmed, it will automatically be regarded as withdrawn by the applicant. There will be no reminder and no invitation. Confirmation of a designation consists of the filing of a notice specifying the designated State concerned (with an indication of the kind of protection or treatment desired) and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 16-month time limit.

REQUIREMENTS REGARDING PRIORITY DOCUMENTS

For applicants who have not yet complied with the requirements regarding priority documents, the following is recalled.

Where the priority of an earlier national, regional or international application is claimed, the applicant must submit a copy of the said earlier application, certified by the authority with which it was filed ("the priority document") to the receiving Office (which will transmit it to the International Bureau) or directly to the International Bureau, before the expiration of 16 months from the priority date, provided that any such priority document may still be submitted to the International Bureau before that date of international publication of the international application, in which case that document will be considered to have been received by the International Bureau on the last day of the 16-month time limit (Rule 17.1(a)).

Where the priority document is issued by the receiving Office, the applicant may, instead of submitting the priority document, request the receiving Office to prepare and transmit the priority document to the International Bureau. Such request must be made before the expiration of the 16-month time limit and may be subjected by the receiving Office to the payment of a fee (Rule 17.1(b)).

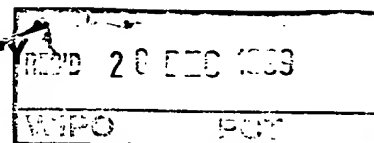
If the priority document concerned is not submitted to the International Bureau or if the request to the receiving Office to prepare and transmit the priority document has not been made (and the corresponding fee, if any, paid) within the applicable time limit indicated under the preceding paragraphs, any designated State may disregard the priority claim, provided that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity to furnish the priority document within a time limit which is reasonable under the circumstances.

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 16-month time limit is the filing date of the earliest application whose priority is claimed.

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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

14

Applicant's or agent's file reference PB751/PCT/RS		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) FOR FURTHER ACTION	
International application No. PCT/EP98/08394	International filing date (day/month/year) 21/12/1998	Priority date (day/month/year) 23/12/1997	
International Patent Classification (IPC) or national classification and IPC A01N57/34		RECEIVED JUL 11 2001 TECH CENTER 1600/2900	
Applicant ALBRIGHT & WILSON UK LIMITED et al.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 5 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 11 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 16/07/1999	Date of completion of this report 11.6.12.99
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Boletti-Cremers, K Telephone No. +49 89 2399 8541 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP98/08394

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*:

Description, pages:

3,4,6-8,10-19 as originally filed

1,2,2a,5,9, as received on 09/11/1999 with letter of 04/11/1999
20-22

Claims, No.:

1-12 as received on 09/11/1999 with letter of 04/11/1999

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JUL 11 2001
TECH CENTER 1600/2900

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-12
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-12
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-12
	No:	Claims	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP98/08394

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP98/08394

The proposed amendments of the original claimed matter, as filed on 04.11.99 by the Applicant, are acceptable under Rule 70.2(c) PCT.
Present claims 1-12 replace the original claims 1-17.

POINT V

The following documents, quoted in the I.S.R., have been considered as relevant for the examination of the present application. Their numbering will be adhered to for the rest of the procedure.

- (1) EP-A-0 385 676
- (2) US-A-3 644 083
- (3) GB-A-2 257 043
- (4) WO-A-91/04668.
- (5) GB-A-2 178 960.

Novelty.

In view of the reformulated scope of the synergistically mixtures and methods for treating aqueous systems, which are now characterised by the explicit presence of the non foaming biopenetrant, the claimed matter can now be regarded as novel with respect to the content of the above named documents.

- (a) Indeed, although (1) refers to a synergy between 2 known biocides (THP and TCMTB), (1) does only teach the synergism between those 2 non penetrant biocides, from which TCMTB is now clearly outside the scope of the reformulated claims on file.

Novelty with respect to the content of that document can thus be acknowledged.

- (b) (2) refers to the use of THP together with organic compounds of trivalent oxygen to impart fire retardant finishes to textiles. Since the reformulated claimed matter now precises the nature of the biopenetrant useful for aqueous treatment, the compositions of (2), which merely encompass, besides THP, a compound which can be melamine, urea, or a condensate of formaldehyde with melamine, do no longer fall within the scope of the compositions and methods on file.

The claimed matter can therefore be regarded as novel vis à vis the content of (2).

- (c) (3) refers to the use of THP with a synergistically active cationic surfactant as a timber preservative .

The quaternary nitrogen compounds referred to in (3) are not polymeric compounds and therefore novelty with respect to the content of (3) can also be acknowledged . Moreover (3) does not concern water treatment .

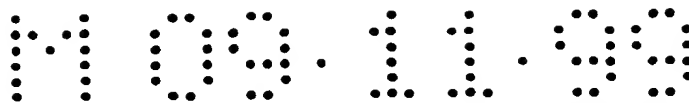
- (d) The novelty of the claimed matter with respect to the content of (4) and (5) can be acknowledged , because none of those documents refers to the use of THP in conjunction with a non surfactant biopenetrant additive for the preparation of a synergetic composition .

Inventive Step .

Out of all the documents quoted above , the only document addressing the problem of water treatments is (5) .

Said document constitutes therefore the most relevant prior art with respect to the invention as claimed.

Since none of the above document (including (5)) teaches the possibility of using non-surfactant biopenetrant in place of a surfactant to enhance the performance of THP as a water treatment biocide and since the examples of the description establish already that the claimed mixtures are superior to mixtures with surfactant in respect of biocidal effect as well as low foaming , the inventive step of the claimed matter with the content of (5) is established .



BIOCIDAL COMPOSITIONS AND TREATMENTS

The present invention relates to synergistic biocidal mixtures of hydroxymethyl phosphonium biocides with certain non-foaming biopenetrants.

GB 2 145 708 describes biocidal uses of tetrakis (hydroxymethyl) phosphonium salts, which, together with their parent base, tris(hydroxymethyl)phosphine, are referred to herein collectively as "THP". US 4 778 813 describes the biocidal use of quaternary ammonium polymers. GB 2 178 960 describes synergism between THP and surfactant. GB 2 228 680 describes synergism between THP and certain aldehydes.

EP 0 385 676 describes compositions which comprise THP, a synergistic amount of a thiocyanate biocide and a glycol ether as solvent for the latter.

US 3644 083 describes the use of THP with nitrogenous organic compounds as flame retardants.

GB 2 257 043 describes the application of THP to wood in conjunction with quaternary surfactants to control sapstain.

THP formulations are increasingly widely used as biocides for water treatment in treating cooling water, process water e.g. in pulp and paper manufacture, drilling fluids and other aerobic water systems, as well as in anaerobic systems such as oil field formation water, injection water, produced water and water used in hydrostatic testing. Advantages include rapid and effective bactericidal activity and environmental acceptability. Particularly in systems where slime forming bacteria proliferate (e.g. in aerobic systems such as cooling water) it has been found desirable to use THP formulations containing synergistic amounts of a surfactant according to GB 2 178 960, in order to improve cost effective biocidal action. It is believed that the surfactant aids the penetration of biomass by the THP. However such formulations cause foaming problems. Attempts to combine THP with other biocides (e.g.

aldehydes), which do not cause foaming, have not been able to provide such effective biocidal action against slime forming bacteria, and/or have detracted from the favourable environmental profile of THP.

We have now discovered that combinations of THP with certain non-surfactant biopenetrants provide strongly synergistic biocidal formulations which give excellent penetration of bacterial slime and improved activity against planktonic bacteria without causing excessive foam. We have further discovered that mixtures of THP with a surfactant, and with a non-surfactant biopenetrant give a marked ternary synergism, permitting improved biocidal efficiency with reduced foaming.

Our invention provides a biocidally synergistic mixture comprising THP and at least one THP-compatible, non-surfactant, biopenetrant synergist together optionally with a surfactant characterised in that the non-surfactant biopenetrant is selected from quaternary ammonium polymers and copolymers, an alkyl benzene or alkyl naphthalene sulphonate having less than 5 aliphatic carbon atoms and/or a phosphono polycarboxylic acid.

According to a second embodiment the invention provides a method of treating aqueous systems contaminated, or liable to contamination, with microbes such as bacteria, fungi or algae which comprises applying thereto separately or together a biocidally active amount of the components of a synergistic mixture of the THP with either a non-surfactant biopenetrant as aforesaid or a syntan.

The aqueous system may, for instance, be contaminated with bacterial slime and/or planktonic bacteria. The invention is of use for treating aerobic systems such as cooling towers and also for anaerobic systems, such as oil wells, e.g. during secondary recovery.

The THP is conveniently present in the formulation as a salt, but is preferably used at a pH sufficient to form the base. The salt is preferably the sulphate, chloride or phosphate. However any water soluble salt may be used including the phosphite, bromide, fluoride, carbonate, acetate, formate, citrate, borate, or silicate. In fact any counter ion which is

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chemically compatible with the THP may be used, the main criteria for selection being economic. Oxidation of THP to tris(hydroxymethyl)phosphine oxide (THPO) should be avoided and oxidising agents for THP are preferably substantially absent. The composition may contain oxygen scavengers to minimise oxidation by atmospheric oxygen. The pH of the composition may be below 3.5 to avoid THPO formation during storage but the pH on addition to aqueous systems is preferably between 3.5 and 9 and more preferably less than 8. e.g. 4 to 7.5. High alkalinity e.g. above 10 is preferably avoided. The pH of the aqueous system may optionally be adjusted by addition of alkali or acid as appropriate.

An important class of hydrotropes for use according to our invention comprises the lower alky aryl sulphonates. Water soluble salts, e.g. sodium, potassium, ammonium or salts of benzene sulphonic, toluene sulphonic, xylene sulphonic, ethyl benzene sulphonic or cumene sulphonic acids are very effective. Generally, alkylbenzene sulphonic acids having up to four or even five aliphatic carbon atoms shown hydrotropicity but not significant surfactancy. Above six aliphatic carbons, e.g. sodium octyl benzene sulphonate, surfactancy predominates over hydrotropicity. Naphthalene sulphonates are also useful as non-surfactant biopenetrants, e.g. alkali metal C₁₋₄ alkyl naphthalene sulphonates. Urea is also an effective hydrotrope.

A further category of non-surfactant biopenetrants comprises syntans. The latter include a variety of resins and prepolymers which are used in the tanning industry as an alternative to tannin or chrome.

Animal skins comprise a layer of collagen, and tanning agents react to cross link reactive sites within the collagen. One effect of this reaction is to increase the minimum temperature at which the leather tends to shrink in hot water.

The biopenetrant synergist is not usually present in a greater weight concentration than the THP, although higher concentrations by weight based on THP, e.g. up to 10:1 or even 100:1 are technically possible but commercially undesirable. The proportion is preferably less than 50% by weight based on the weight of THP, more usually less than 20%, typically less than 10%, especially less than 5%. Although very small amounts may be effective we prefer to use proportions of biopenetrant greater than 0.1% based on the weight of THP, usually greater than 0.5%, especially greater than 1%.

The biocide is typically supplied as a 10 to 75%, e.g. 20 to 60%, especially 30 to 50% by weight aqueous solution of THP containing from 0.1 to 10%, e.g. 0.2 to 5%, especially 0.5 to 2% of the synergist, based on the total weight of the solution.

Alternatively the composition may be supplied as a solid formed by coating THP onto, or absorbing it into, a powdery or granular or porous acid substrate such as adipic acid.

The mixture is typically used at a dosage of 1 to 1500ppm by weight THP based on the weight of water to be treated, usually 2 to 500, especially 5 to 250, e.g. 10 to 150.

According to a particular embodiment it has been found that mixtures of the aforesaid biopenetrant synergists with surfactants and THP salts provide an enhanced synergism. Such mixtures can provide even more effective biocidal activity, at substantially lower levels of both biocide and surfactant than are required for conventional mixtures of THP salts and surfactant.

Our invention accordingly further provides a biocidally synergistic mixture comprising:
(A) THP; (B) at least one non-surfactant biopenetrant as aforesaid; and (C) surfactant.

The invention further provides a method of treating water with a biocidally active amount of said synergistic mixture.

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The example of the invention also showed superior performance to conventional THP surfactant formulations, to WSCP alone and to THP alone in reducing planktonic bacteria.

The example gave less than half the foaming observed using surfactant containing formulations.

Example 2

An aqueous solution comprising 50% THPS and 2% WSCP was added to alginate beads infected with sulphate reducing bacteria. When dosed at 250ppm, solution gave a 100 fold reduction in bacterial counts, compared with a control, after two weeks incubation.

At 500ppm the solution gave a total kill.

Example 3

The alginate bead test of examples 2 and 3 was repeated using sodium naphthalene sulphonate/formaldehyde condensate as the synergist. As 250ppm the solution gave a 100 fold reduction in bacterial counts after two weeks incubation. At 500ppm the solution gave a total kill. The volume of foam generated when air was bubbled through the system containing 750ppm of the active biocidal mixture was half that using THP alone.

Example 4

The alginate bead test of Example 1 was repeated using generally heterotroph bacteria and a residence time of two hours. For comparison we used the most commonly used commercial THP biocide product which is an aqueous solution comprising 50% THPS and 2% of an anionic surfactant available commercially under the Registered Trade Mark "DOWFAX" 2A1.

Various mixtures each comprising 50% THPS and 2% of biopenetrant were compared at 250ppm and at 125ppm dosage. The log reduction in bacterial counts is given in the table.

TABLE

BIOPENETRANT	FUNCTIONALITY	LOG REDUCTION
Comparative	Surfactant	
250ppm		3.7
125ppm		3.0
Sodium xylene sulphonate	Hydrotrope	
250ppm		4.7
125ppm		2.7
THP/urea condensate	"Syntan"	
250ppm		5.00
125ppm		3.70
Formaldehyde/dihydroxyphenylsulphono poly condensate	"Syntan"	
250ppm		4.0
125ppm		2.7
Urea	Hydrotrope	
250ppm		6.7
125ppm		4.0

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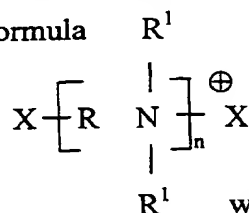
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In each case the biopenetrant of the invention showed improved biocidal activity compared with the surfactant in the comparative example, and gave substantially less foaming.

CLAIMS

1. A biocidally synergistic mixture comprising THP, at least one THP-compatible non-surfactant biopenetrant and, optionally, a surfactant, characterised in that said biopenetrant is a polymer or copolymer, having a plurality of quaternary ammonium groups, and/or an alkyl benzene or alkyl naphthalene sulphonate having less than 5 aliphatic carbon atoms, and/or a phosphono polycarboxylic acid.
2. A composition according to claim 1 comprising as biopenetrant a compound having a polymeric cation with the formula



wherein each R is a divalent organic group constituting, with the ammonium group, a monomeric residue, or is separately selected from two or more comonomeric residues and each R is an alkyl or hydroxyalkyl group, X is hydrogen or a monovalent inorganic or organic end capping unit and n is from 3 to 3000.

3. A composition according to claim 1 wherein the non-surfactant biopenetrant is a methylated polyethylene polyamine comprising a polymeric cation of the formula:



where n is from 2 to 10.

4. A composition according to any foregoing claim wherein the non-surfactant biopenetrant comprises poly[oxyethylene(dimethylininio)ethylene (dimethylininio)ethylene dichloride].

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12. A method according to any of claims 8 to 11 wherein the total weight proportion of THP and biopenetrants dosed to the system is from 2 to 1000ppm

5. A composition according to any foregoing claim consisting of an aqueous solution wherein the concentration of THP is from 10 to 75% by weight of the solution and the concentration of non-surfactant biopenetrant synergist is from 0.1 to 10% by weight of the solution.
6. A composition according to any foregoing claim additionally comprising a surfactant.
7. A composition according to claim 14 wherein the surfactant is present in a weight proportion of from 50:1 to 1:200 based on the weight of the THP.
8. A method for treating aqueous systems to prevent, inhibit or remove microbial contamination, which comprises adding thereto, together or separately, the components of a biocidally synergistic mixture comprising THP, at least one THP-compatible non-surfactant biopenetrant and, optionally, a surfactant, characterised in that said biopenetrant comprises a polymer or copolymer, having a plurality of quaternary ammonium groups, an alkyl benzene or alkyl naphthalene sulphonate having less than 5 aliphatic carbon atoms and/or a syntan.
9. A method according to claim 8 wherein the non-surfactant biopenetrant comprises a condensate of formaldehyde, acetone and/or THP with a phenol, aryl sulphonate, sulphone, sulphonamide, urea, melamine, C_{1 to 14} alkyl amine or dicyandiamide.
10. A method according to claim 8 or 9 wherein said biopenetrant comprises urea and/or a urea THP condensate.
11. A method for treating aqueous systems to prevent, inhibit or remove microbial contamination, which comprises adding thereto, together or separately, the components of a composition according to any claims 1 to 7.